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### Corrosion behavior of Ni-based superalloys in molten FLiNaK salts

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#### ABSTRACT

High temperature corrosion tests of alloys, Inconel 718, Inconel C-276 and Nimonic 80A, were performed at 680 °C in molten alkali fluoride salt (LiF–NaF–KF: 46.5–11.5–42%) environment. These experiments were carried out from 8 to 48 hours of immersion period in an attempt to understand the corresponding corrosion behaviour of the alloys at different times. Corrosion was noted to occur predominantly by dealloying of Cr from the alloys, an effect that was particularly pronounced at the grain boundaries of these alloys. Microstructural examination showed the depletion of Cr near surface of the alloys and also revealed mild intergranular corrosion at early stage of corrosion test. But in general all three alloys performed well and showed reasonably low corrosion rates in aggressive FLiNaK environments.

Keywords: hot corrosion, oxidation, structural materials, oxide scales, molten systems

#### INTRODUCTION

The use of molten salt technology as a working fluid has a proven success in many industrial applications. In fact, molten salts have been proposed for use in many energy conversion technologies mainly due to their potential as heat transfer agents and industrial liquid fuels. Molten fluoride salts possess several important properties: excellent thermal conductivity. stability at desired working temperatures, high boiling point, high specific heat and low viscosity<sup>1</sup>. Molten fluoride salts such as LiF-NaF-KF (FLiNaK) and LiF-BeF<sub>2</sub> (FLiBe) have been proposed for use as primary and secondary reactant coolants in molten salt reactors (MSR)<sup>2</sup>, Advanced High-Temperature Reactor (AHTR)<sup>3</sup> and in solar power towers<sup>4</sup>. However, compatibility of molten fluoride salts with the structural alloys and materials corrosion has been of real concern at such temperatures (600-900 °C). Hence, the material development and the corrosion studies turn out to be an essential part of research. Materials derive corrosion resistance by formation of passive oxide film but in molten fluoride salt systems, passive oxide films are unstable and once the film is vanished, the least noble alloving element is selectively attacked by dissolution<sup>5,6</sup>. These three type of corrosion mechanisms are proposed for materials in static molten fluoride salts: intrinsic corrosion, corrosion by impurities, and galvanic corrosion<sup>7</sup>. The team Olson<sup>2</sup> and Ouyang and co-workers<sup>8-9</sup> presented a good selection of alloys studied in FLiNaK. It has been a constant rise in corrosion investigations reported in various molten salt environments from both theoretical and experimental viewpoints. However, corrosion studies of superalloys in molten fluoride salts are limited to only a handful of research teams globally and only few of them involved a varied range of alloys<sup>8-11</sup>. A more detailed and comprehensive literature review on high temperature corrosion behaviour of superalloys in molten salts was recently published by us<sup>12</sup>, in an effort to give an in-depth insight of the recent developments that have occurred in the latter part of the last decade.

In this study, we investigated corrosion characteristics of alloys Inconel 718, Inconel C-276 and Nimonic 80A in high temperature molten FLiNaK environments at an ambient temperature of 700 °C. These experiments were carried out from 8 to 48 hours of immersion period in an attempt to understand the corresponding corrosion behaviour of the tested alloys at given time intervals, respectively. Various microstructural characterisation techniques were used to reveal the cross-sectional morphologies of the corroded samples and to evaluate corrosion attack depth.

#### **EXPERIMENTAL PROCEDURE**

#### Materials and preparations

Three Ni based alloys Inconel 718, Inconel C-276 and Nimonic 80A (supplier Bibus Metals s.r.o, Czech Republic) were selected as the target materials for corrosion tests. The composition of the tested alloys are listed in Table-1 below. The samples were cut into 2 mm thick discs by a boron nitride blade (CBN-blade) on precision cutter Isomet 5000 (Buehler, USA). The samples were then prepared by mechanical polishing and grinding by Tegrapol - 25 (Struers, USA) with a diamond suspension (1µm). Then, the samples were ultrasonically cleaned in acetone and deionized water; and transferred to glove box in a desiccator. The exact dimensions of each sample were measured using a micrometre screw gauge (with a precision of 0.01 mm) and the weights before and after the experiment were recorded with highly precise KERN analytical weighing balance (KERN ABT Merck, Germany).

#### Table 1: Compositions of Alloys

Alloy/ composition (wt.%)	Ni	Cr	Fe	Со	Мо	W	AI	Mn	Ti	Si	Nb	Cu
Nimonic 80A	76	19.5	0	0	-	-	1.4	-	2.4	1	-	-
Inconel C-276	57	16	5	3	16	4	-	1	-	0	-	-
Inconel 718	54	18	18.5	1	3	-	0.5	1	1	0	5	0

FLiNaK salts were considered in this study because of its exceptional properties (Table 2). Eutectic FLiNaK salts were composed of LiF (Ubichem, UK, purity 99%), NaF (Merck, Germany, purity 99%), and KF (Fluka Chemicals, UK, purity 99.5%) at ratios of 46.5–11.5–42%, respectively. Salts were dried for 48 hours in a vacuum drying chamber (JAVOZ, Czech Republic) at 130 °C, then stored and mixed in a glove box (H2O and O2 < 1 ppm) prior to the corrosion experiments.

Salt compounds [mol%]	46.5 LiF 11.5 NaF 42 KF
Melting point [°C]	454
Boiling point [°C]	1570
Heat capacity [J / g / °C]	1.88
Thermal conductivity [W m <sup>-1</sup> K <sup>-1</sup> ]	0.92
Density [g cm <sup>-3</sup> ]	2.02
Viscosity [cP]	2.9

#### Table 2: Properties of FLiNaK (eut)

#### Immersion method

Weight loss for the Ni-alloy coupons was observed by immersion method for 8 to 48 hours period in molten FLiNaK. The coupons were prepared as described in the section above. The crucibles (sintered  $Al_2O_3$ , 99%) were dried at 105 °C before filling. For each individual experiment, 50 g of the mixture of FLiNaK (eut) were weighed, loaded into the crucible and homogenized in a glove box under an inert atmosphere. Then, the coupons were immersed and resulted weight loss was measured and reported accurately. Weight loss measurements were performed in the sets of three and repeated three times to confirm the reproducibility of results.

#### Microstructural characterization

Scanning electron microscopy (SEM) (JEOL7600F, Japan) in combination with Electron dispersive spectroscopy (EDS) (Oxford Instruments Ltd., UK) was used for the superficial and cross-sectional microstructure observation. Electron gun voltage was set to 15kV to assure sufficient extraction energy and to quantify chemical composition; Co standard was used before measurement. The samples for microstructural observation were prepared via standard metallographic methods such as grinding and polishing. No additional etching was used.

#### RESULTS

Nimonic 80A, Inconel C276 and Inconel 718 alloys have been acquired and tested in molten FLiNaK salt mixture at 680 °C for the period of 8h, 24h, 30h and 48h respectively.

Fig. 1 shows the cross-sectional morphologies of the tested alloys in molten FLiNaK for immersion of 24 h for comparisons. The observed oxidation of materials near the surface after corrosion tests varies considerably for the tested alloys. Although, no significant intergranular attack was witnessed for any of the alloys examined for up to 24 h immersion period.



Fig. 1. Cross-sectional SEM images of the microstructure of the corrosion layer of studied alloys in molten FLiNaK after 24 h of immersion period; Nimonic 80A (a), Inconel C276 (b) and Inconel 718 (c).



Ni Ka1

Ni Ka1

Ni Ka1



(a)
 (b)
 (c)
 Fig. 2. Cross-sectional microstructures and EDS elemental mapping of Ni, Cr and O in the corrosion layer of studied alloys in molten FLiNaK after 24 h of immersion period; Nimonic 80A (a), Inconel C276 (b) and Inconel 718 (c).

Fig. 2 shows the cross-sectional microstructure and EDS elemental mapping of the tested alloys after 24 h immersion testing at 680°C in molten FLiNaK. The images show that clear oxide layers were formed at the surface of all the examined alloys. However, the width of the oxide layer varies in size; it is approximately 4  $\mu$ m in case of Nimonic 80A, less than 2  $\mu$ m for Inconel C 276 and about 8  $\mu$ m for Inconel 718. Beneath these oxide layers, distinct depleted zones were observed for the tested specimens as can be seen in Fig. 2.



## Fig.3. Cross-sectional microstructures of Nimonic 80A and related EDS elemental line scan through corrosion layer and base metal

Table 3. Chemical composition of the Nimonic 80A in wt. % in different areas; oxide layer, depletion zone and base metal.

Nimonic 80A	0	AI	Ti	Cr	Ni
Oxide layer	51.6	1.2	0.9	44.9	1.4
Depletion zone	-	0.3	0.3	8.0	91.5
Base metal	-	1.6	2.4	19.8	76.2



Fig.4. Cross-sectional microstructures of InconelC276 and related EDS elemental line scan through corrosion layer and base metal

Table 4. Chemical composition of the Inconel C276 in wt. % in different areas; oxidelayer, depletion zone and base metal.

Inconel C276	0	AI	Cr	Fe	Ni	Мо	W
Oxide layer	48.7	4.7	21.1	2.2	20.1	3.2	2.5
Depletion zone	-	-	3.4	7.3	71.4	15.1	2.8
Base metal	-	-	15.2	5.9	56.8	17.8	4.3



Fig.5. Cross-sectional microstructures of Inconel718 and related EDS elemental line scan through corrosion layer and base metal

Inconel 718	0	Al	Ti	Cr	Fe	Ni
Oxide layer	42.9	1.1	0.6	43.1	3.6	8.4
Depletion zone	-	-	-	2.6	23.4	72.1
Base metal	-	0.6	1.0	19.8	19.5	56.1

# Table 5. Chemical composition of the Inconel 718 in wt. % in different areas; oxidelayer, depletion zone and base metal.

From Fig.3-5 and Table 3-5, it's clear that the most reactive constituents near the surface (Cr) were quickly dissolved into molten salt environments through formation of metal fluoride. That created depletion zone of Cr in the vicinity of the surface which is also confirmed by the above mentioned tables. To sum up, the above results suggest that Cr must migrate to the alloy surface to sustain attack from the FLiNaK salts.

#### CONCLUSIONS

The corrosion behaviour of the Ni-based superalloys was investigated in FLiNaK with high temperature corrosion environment. The corrosion resistance of the Ni-based superalloys in the molten FLiNaK salt in high temperature corrosion environments was strongly related to the phase composition of the materials. Cr-rich oxide layers were formed and may have proved vital as further internal corrosion was retarded or slowed significantly for longer immersion hours.

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